

CORRECTED VERSION

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
24 June 2004 (24.06.2004)

PCT

(10) International Publication Number  
WO 2004/052977 A1

- (51) International Patent Classification<sup>7</sup>: C08K 5/04,  
C08L 27/06 // (C08K 5/04, 5:1515, 5:101)
- (21) International Application Number:  
PCT/BR2002/000175
- (22) International Filing Date: 6 December 2002 (06.12.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (71) Applicant (for all designated States except US): COGNIS BRASIL LTDA. [BR/BR]; Av. das Nações Unidas, 10989-4° andar, CEP-04578-000 São Paulo, SP (BR).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): BUENO DE ALMEIDA, Wanderson [BR/BR]; Rua República do Libano, 314, Apto. 22, Jardim Osvaldo Cruz, CEP-12216-590 São José dos Campos, SP (BR). BRAGA, Katia [BR/BR]; Rua Guido Zecca, 38, Esplanada do Sol, CEP-12244-680 São José dos Campos, SP (BR). SOUSA SALES, Henrique, Jorge [BR/BR]; Avenida Dr. João
- (74) Agent: DANNEMANN, SIEMSEN, BIGLER & IPANEMA MOREIRA; Caixa Postal 2142, Rua Marquês de Olinda, 70, CEP-22251-040 Rio de Janeiro, RJ (BR).
- (81) Designated States (national): BR, US.
- (84) Designated States (regional): European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR).
- Published:  
— with international search report
- (48) Date of publication of this corrected version:  
10 September 2004
- (15) Information about Correction:  
see PCT Gazette No. 37/2004 of 10 September 2004, Section II
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PLASTICIZED POLY VINYL CHLORIDE COMPOSITIONS

(57) Abstract: The invention relates to plasticized poly vinyl chloride compositions comprising (a) 100 parts by weight of at least one poly vinyl chloride resin and (b) 0,1 to 200 parts by weight of a plasticizer compounded with said at least one poly vinyl chloride resin, wherein said plasticizer comprises (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear or branched.

WO 2004/052977 A1

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
24 June 2004 (24.06.2004)

PCT

(10) International Publication Number  
WO 2004/052977 A1

(51) International Patent Classification?: C08K 5/04,  
C08L 27/06 // (C08K 5/04, 5:1515, 5:101

Katia [BR/BR]; Rua Guido Zecca, 38, Esplanada do Sol,  
CEP-12244-680 São José dos Campos, SP (BR). SOUSA  
SALES, Henrique, Jorge [BR/BR]; Avenida Dr. João  
Batista de Queiroz Jr., apto. 74, Jardim das Indústrias,  
CEP-12240-000 São José dos Campos, SP (BR).

(21) International Application Number:  
PCT/BR2002/000175

(22) International Filing Date: 6 December 2002 (06.12.2002)

(74) Agent: DANNEMANN, SIEMSEN, BIGLER &  
IPANEMA MOREIRA; Caixa Postal 2142, Rua Marquês  
de Olinda, 70, CEP-22251-040 Rio de Janeiro, RJ (BR).

(25) Filing Language: English

(26) Publication Language: English

(81) Designated States (*national*): BR, US.

(71) Applicant (*for all designated States except US*): COG-  
NIS BRASIL LTDA. [BR/BR]; Av. das Nações Unidas,  
10989-4º andar, CEP-04578-000 São Paulo, SP (BR).

(84) Designated States (*regional*): European patent (AT, BE,  
BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT,  
LU, MC, NL, PT, SE, SI, SK, TR).

Published:

— with international search report

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): BUENO DE  
ALMEIDA, Wanderson [BR/BR]; Rua República  
do Libano, 314, Apto. 22, Jardim Osvaldo Cruz,  
CEP-12216-590 São José dos Campos, SP (BR). BRAGA,

*For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.*

(54) Title: PLASTICIZED POLY VINYL CHLORIDE COMPOSITIONS

(57) Abstract: The invention relates to plasticized poly vinyl chloride compositions comprising (a) 100 parts by weight of at least one poly vinyl chloride resin and (b) 0,1 to 200 parts by weight of a plasticizer compounded with said at least one poly vinyl chloride resin, wherein said plasticizer comprises (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear or branched.

WO 2004/052977 A1

**Title: "Plasticized poly vinyl chloride composition"****Field of the Invention**

5 The invention relates to plasticized poly vinyl chloride compositions comprising at least one poly vinyl chloride resin and a special plasticizer compounded with said at least one poly vinyl chloride resin.

**Description of the Related Art**

10 **WO 01/98404** discloses a plasticized vinyl chloride composition comprising (a) at least one vinyl chloride resin and (b) a plasticizer compounded with (a) wherein said plasticizer comprises a fatty acid product derived from a vegetable oil having at least 80% by weight of unsaturated fatty acids, wherein said fatty acids are substantially fully esterified with a monool or a polyol, and said esterified unsaturated fatty acids have been substantially fully epoxidized.

15 In an article entitled "Use of esterified rapeseed oil as plasticizer" in plastics processing" by Johannes Wehlmann it is mentioned that in most cases phthalic acid esters, especially dioctyl phthalate (DOP), are used as plasticizers for poly vinyl chloride (PVC) resins (see **Fett/Lipid 101, 1999, No. 6, pages 249-256**). However, phthalate plasticizers are criticized because of their environmentally harmful action. The author then describes the use of rape methyl ester as plasticizer.

**Detailed Description of the Invention**

25 It was an object of the present invention to provide plasticizers for plastics, especially PVC, which overcome the difficulties and disadvantages of the plasticizers of the prior art. It was a further object of the invention that PVC plastisol formulations based on these plasticizers show a reduced viscosity compared with formulations based on phthalic ester type plasticizers like dioctyl phthalate (DOP). As it is known to the artisan plastisols are dispersions of plastics, especially PVC, in plasticizers.

30 According to the invention this is achieved by **plasticized poly vinyl chloride compositions** comprising (a) 100 parts by weight of at least

one poly vinyl chloride resin and (b) 0,1 to 200 parts by weight of a plasticizer compounded with said at least one poly vinyl chloride resin, wherein said plasticizer comprises (i) esters of fatty acids with 8 to 14 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically  
5 unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear or branched.

In a preferred embodiment of the invention the plasticized poly  
10 vinyl chloride compositions are free of phthalic ester type plasticizers and especially free of dioctylphthalate (DOP).

In another embodiment of the invention the weight ratio of compounds (i) and (ii) is within the range 90 : 10 and 50 : 50 and especially within the range 65 : 35 and 55 : 45.

15 The invention also relates to **plasticizer compositions** for poly vinyl chloride resins comprising (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16  
20 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear or branched. Preferably these plasticizer compositions are free of dioctylphthalate. In one embodiment these plasticizer compositions contain compounds (i) and (ii) in an amount that the weight ratio of compounds (i) and (ii) is within the range 90 : 10 and 50 : 50 and especially within the range 65 : 35 and 55 : 45. In another preferred embodi-  
25 ment these plasticizer compositions contain exclusively compounds (i) and (ii).

The invention also relates to the use of compositions comprising  
30 (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the pro-

viso that these fatty acids can be saturated or olefinically unsaturated, linear or branched as **plasticizers for poly vinyl chloride resins**. As stated above the compositions are preferably free of are free of phthalic ester type plasticizers.

5           As also stated above the compositions preferably contain compounds (i) and (ii) in an amount that the weight ratio of compounds (i) and (ii) is within the range 90 : 10 and 50 : 50 and especially within the range 65 : 35 and 55 : 45. Those compositions which exclusively contain compounds (i) and (ii) are preferred for the use as plasticizers for poly vinyl chloride resins.

10    **Examples**

**IES** = Isobutyl epoxy stearate

**IFAME** = Mixture of methyl esters of fatty acids. The distribution of the fatty acid individuals in these methyl esters was (% means mole-%):  
15   Straight chain C12 = 0.3%, branched chain C14 = 0.4%, straight chain C14 = 1.0%, branched chain C16 = 3.7% , straight chain C16 = 4.9%, branched chain C18 = 61.4%, straight chain C18 = 4.6%, cyclic C18 = 17.5%, straight chain C20 = 0.1%, aromatic C18 = 6.1%.

**Filler** = Calcium Carbonate (Calcit)

**Stabilizer** = Stabiol CZ 3083 (Liquid Ca/Zn Stabilizer commercially available from COGNIS)

20           **PVC** = Poly vinyl chloride produced by emulsion polymerization (Solvic 374 MB commercially available from SOLVAY)

**Example 1**

          (PVC Ball formulation)

25           The following compounds were mixed together in a conventional mixer:

PVC	100 phr
IES	60 phr
IFAME	40 phr
30   Filler	90 phr
Stabilizer	1 phr

          The abbreviation phr means "parts per hundred resin" and is

known to the man skilled in the art.

The viscosity of the formulation was measured according to Brookfield (Spindle 5 at 20 rpm). It was 36.000 cps. The value of the viscosity is much lower compared to the formulation of comparative example 1 which is based on dioctyl phthalate as plasticizer.

The formulation was then transferred into a ball by rotational moulding at 180 °C. The shore A hardness of the ball was measured. It was 54,8. The value of the shore A hardness is nearly the same as the shore A hardness of the ball in comparative example 1. This shows that the IES/IFAME mixture is as good as plasticizer as the "classical" dioctylphthalate.

#### **Comparative Example 1**

(PVC Ball formulation)

The following compounds were mixed together in a conventional

mixer:

PVC	100 phr
<b>dioctyl phthalate</b>	100 phr
Filler	90 phr
Stabilizer	1 phr

The viscosity of the formulation was measured according to Brookfield (Spindle 7, 5 rpm). It was 125.400 cps

The formulation was then transferred into a ball by rotational moulding at 180 °C. The shore A hardness of the ball was measured; it was 54,0.

## Claims

1. Plasticized poly vinyl chloride compositions comprising (a) 100 parts by weight of at least one poly vinyl chloride resin and (b) 0,1 to 200 parts by weight of a plasticizer compounded with (i) esters of fatty acids with  
5 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear or branched.

10 2. Compositions according to claim 1 wherein said plasticized poly vinyl chloride compositions are free of phthalic ester type plasticizers.

3. Composition according to claim 1 wherein the weight ratio of compounds (i) and (ii) is within the range 65 : 35 and 55 : 45.

15 4. Plasticizer compositions for poly vinyl chloride resins comprising (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear  
20 or branched.

5. Compositions according to claim 4 with the proviso that the compositions are free of phthalic ester type plasticizers.

6. Compositions according to claim 4 with the proviso that the weight ratio of compounds (i) and (ii) is within the range 65 : 35 and 55 : 45.

25 7. Compositions according to claim 4 with the further proviso that the compositions contain exclusively compounds (i) and (ii).

8. The use of compositions comprising (i) esters of fatty acids with 8 to 24 carbon atoms and isobutanol with the proviso that the fatty acids can be saturated or olefinically unsaturated, linear or branched and contain  
30 at least one epoxy group per molecule and (ii) one or more methyl esters of fatty acids with 16 to 18 carbon atoms with the proviso that these fatty acids can be saturated or olefinically unsaturated, linear or branched as plastici-

zers for poly vinyl chloride resins.

9. The use according to claim 8 with the proviso that the compositions are free of phthalic ester type plasticizers.

10. The use according to claim 8 with the proviso that the weight  
5 ratio of compounds (i) and (ii) is within the range 65 : 35 and 55 : 45.

11. The use according to claim 8 with the further proviso that the compositions contain exclusively compounds (i) and (ii).



## INTERNATIONAL SEARCH REPORT

International application No

/BR 02/00175

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K5/04 C08L27/06 //(C08K5/04, 5:1515, 5:101)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 934 689 A (SWIFT & CO) 21 August 1963 (1963-08-21) claims 1,8 examples IV-VI	1-11
A	US 2 964 484 A (OHLSON JOHN L ET AL) 13 December 1960 (1960-12-13) examples	1-11
A	EP 0 337 237 A (NEYNABER CHEMIE GMBH) 18 October 1989 (1989-10-18) claims 1,2	1-11
A	DE 38 39 418 A (CIBA GEIGY AG) 8 June 1989 (1989-06-08) claims 1,11,13	1-11
	--- -/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the International filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the International filing date but later than the priority date claimed

\*T\* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*G\* document member of the same patent family

Date of the actual completion of the international search

29 July 2003

Date of mailing of the International search report

06/08/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Rose, E

## INTERNATIONAL SEARCH REPORT

International Application No

/BR 02/00175

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2001/044486 A1 (WESCH KARL) 22 November 2001 (2001-11-22) claims 1,2,7 -----	1-11
A	GB 1 341 623 A (DEGUSSA) 25 December 1973 (1973-12-25) column 1, line 20 -----	1-11
A	US 4 060 508 A (SUGAHARA YUJIRO ET AL) 29 November 1977 (1977-11-29) claims 1,9,17,29 -----	1-11
A	US 3 291 629 A (MAGNE FRANK C ET AL) 13 December 1966 (1966-12-13) claim 1 -----	1-11

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Publication No

5/BR 02/00175

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 934689	A	21-08-1963	DE 1295820 B FR 1254722 A US 3377304 A	22-05-1969 24-02-1961 09-04-1968
US 2964484	A	13-12-1960	BE 560432 A FR 1186294 A GB 861971 A GB 877133 A GB 877136 A GB 877135 A NL 110976 C NL 220398 A NL 302893 A NL 302894 A US 3042692 A US 3006936 A US 3035069 A	19-08-1959 01-03-1961 13-09-1961 13-09-1961 03-07-1962 31-10-1961 15-05-1962
EP 0337237	A	18-10-1989	DE 3812014 A1 BR 8901687 A EP 0337237 A1 JP 1311151 A	26-10-1989 21-11-1989 18-10-1989 15-12-1989
DE 3839418	A	08-06-1989	DE 3839418 A1 FR 2623514 A1 GB 2212808 A , B IT 1227542 B JP 1168747 A	08-06-1989 26-05-1989 02-08-1989 15-04-1991 04-07-1989
US 2001044486	A1	22-11-2001	DE 19509085 A1 AT 231174 T BR 9607664 A CA 2215675 A1 DE 59610056 D1 WO 9628505 A1 EP 0815167 A1 JP 11502240 T ZA 9602143 A	19-09-1996 15-02-2003 16-06-1998 19-09-1996 20-02-2003 19-09-1996 07-01-1998 23-02-1999 16-09-1996
GB 1341623	A	25-12-1973	DE 2009047 A1 AT 305962 B BE 763422 A1 CA 933938 A1 CH 567009 A5 FR 2079133 A5 NL 7100320 A , B ,	02-09-1971 26-03-1973 24-08-1971 18-09-1973 30-09-1975 05-11-1971 30-08-1971
US 4060508	A	29-11-1977	JP 1106397 C JP 51057749 A JP 52032899 B DE 2551220 A1 FR 2291246 A1 GB 1504999 A NL 7513344 A	30-07-1982 20-05-1976 24-08-1977 15-07-1976 11-06-1976 22-03-1978 18-05-1976
US 3291629	A	13-12-1966	US 3219664 A US 3312561 A US 3379551 A	23-11-1965 04-04-1967 23-04-1968